

REACTIONS IN THE RESERVOIR ROCK OF THE HONTOMIN SITE: EXPERIMENTS AND MODELING

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INTRODUCTION

The repository rocks for CO₂ injection at Hontomín are dominantly limestones and dolostones, with clays containing evaporites at the bottom (Keuper). The seal on top of the reservoir is composed mainly of shales and marls, with chlorite and illite as the dominant clay minerals. With these lithologies, it is expected that the composition of the brine in the reservoir will be at equilibrium with calcite, dolomite and anhydrite.

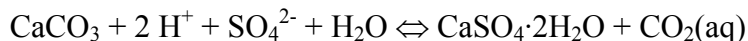
In essence, the geological carbon storage concept consists of injecting supercritical CO₂ into a deep saline aquifer (CO₂ should be in supercritical state to ensure a high density, around 800 kg/m³, and an efficient use of pore space). This requires pressures nearing 100 bar, which explains why injection needs to be deep.

Supercritical CO₂ is lighter and much less viscous than resident saline water. Therefore, it will tend to float until it reaches a low permeability, high entry pressure, mechanically stable caprock that traps it. As a result, a CO₂ phase bubble will tend to form at the aquifer top. At the injection pressure, CO₂ is quite soluble (around 3% in mass; Garcia, 2003). Therefore, it will dissolve. At first, dissolution is limited by diffusion and dispersion away from the CO₂ bubble. However, as time passes, unstable gravity fingers develop below the CO₂ bubble because CO₂-saturated brine is denser than resident brine. The onset of convection as a transport mechanism increases mineral dissolution rates significantly (Riaz et al, 2006). The coupling of flow and chemical reaction can significantly modify the original porosity, permeability and degree of heterogeneity of the rock (e.g. formation of wormholes). Therefore, there is a need to quantify the mineral reaction rates in the rock, the nature of the secondary minerals precipitating, the volumes of reaction and the consequent changes in porosity. To this end, we have initiated a laboratory program centered on reactions in the reservoir rocks.

RESULTS AND DISCUSSION

Experimental work has started with the study of the kinetics of the dissolution of calcite coupled to the precipitation of gypsum. The injection of CO₂ will cause the formation of CO₂-rich acid brines, which will induce the dissolution of the carbonate minerals. Since the brine contains

sulfate (from the dissolution of evaporites), gypsum (or anhydrite at depth) will precipitate, which may cover the surface of the dissolving carbonate causing its passivation.



The first experiments have been conducted at room T and P_{CO_2} . The dissolution of calcite and precipitation of gypsum is studied by means of flow-through experiments.

An acidic solution (H_2SO_4 , pH 2.5) at equilibrium with gypsum is continually injected into a cell containing a known mass of calcite, with a grain size between 1 and 2 mm. Knowing the dissolution rate law for calcite (e.g. Palandri and Kharaka, 2004), its surface area ($0.5 \text{ m}^2/\text{g}$, measured by BET), the volume of solution in the cell (40 mL) and the flow rate (0.035 mL/min), it is possible to calculate the expected evolution of the solution composition at the outlet of the reaction cell. The calculated evolution of solution composition overestimates the dissolution rate of calcite (large increase in pH and Ca concentration). Moreover, a rapid decrease in sulfate concentration is caused by the precipitation of gypsum. Actually the model predicts the complete dissolution of calcite ($t \approx 750 \text{ h}$).

A model refinement requires the reactive surface area of calcite to be decreased until a match between model and experimental results is achieved. The reason for this apparently small reactive surface area probably resides in the effect caused by gypsum precipitating directly on the surfaces of the calcite grains, causing a passivation of the reacting calcite. The evolution of solution composition indicates that the ratio between the volumes of gypsum precipitated and calcite dissolved equals 1.4 ($V_{\text{gyp}}/V_{\text{cc-dis}} = 1.4$), which would translate into a decrease in porosity of the rock matrix.

These results clearly show that even for such a simple system, reaction rates (including the important passivation effects) have to be studied first in the laboratory. Otherwise, model predictions may be significantly off.

References

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